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## Nanoparticles and Polymers. 'Bricks and Mortar' Self-Assembly of Nanostructures

Andrew Boal, Faysal Ilhan, Vincent Rotello,\* Thomas Russell<sup>1</sup>  
 Dept. of Chemistry, <sup>1</sup>Dept. of Polymer Science and Engineering,  
 University of Massachusetts, Amherst, MA 01003 USA

### ABSTRACT

Polymers provide a useful tool for the controlled assembly of colloidal nanoparticles. We have developed a "bricks and mortar" strategy in which colloidal gold particles functionalized with recognition elements serve as the bricks and polymers bearing complementary functionality serve as mortar to hold together the nanoparticles. In this methodology, the conformational flexibility of the polymer compensates for irregularities in the size and shape of the aggregate structure. We have used this method to create discrete micrometer-scale spherical assemblies based on 2 nm gold nanoparticles. Both the size and shape of these assemblies can be controlled, providing spherical assemblies ranging from 50 nm to 1500 nm, as well as network structures.

### DISCUSSION

To provide a general means for the controlled self-assembly of nanoparticles, we have developed a "bricks and mortar" approach. In this strategy, colloidal gold particles functionalized with recognition elements serve as the bricks, while polymers bearing complementary functionality serve as mortar, holding together the colloidal particles. Using this strategy, the conformational flexibility of the polymer compensates for irregularities in the size and shape of the aggregate structure, allowing the efficient propagation of order during the self-assembly process.<sup>1</sup>

Complementarity between colloid and polymer was achieved using diaminotriazine-thymine three-point hydrogen bonding interaction (Figure 1a). For the polymer component, diaminotriazine-functionalized polystyrene **1** was employed (Figure 1b).<sup>2</sup> The required thymine-functionalized colloids were synthesized starting with ~2 nm gold particles covered with an octanethiol self-assembled monolayer (SAM). Thiol place-exchange with thymine-functionalized alkanethiol **5** then provided the derivatized colloid **Thy-Au** (Figure 2). To provide a control system which cannot participate in hydrogen bonding, the highly analogous **MeThy-Au** was prepared in a similar fashion.

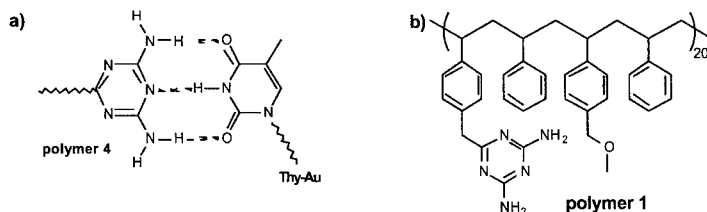


Figure 1. Recognition motif and polymer 'mortar'. a) Diaminotriazine-thymine recognition b) Triazine-functionalized random copolymer **1**.

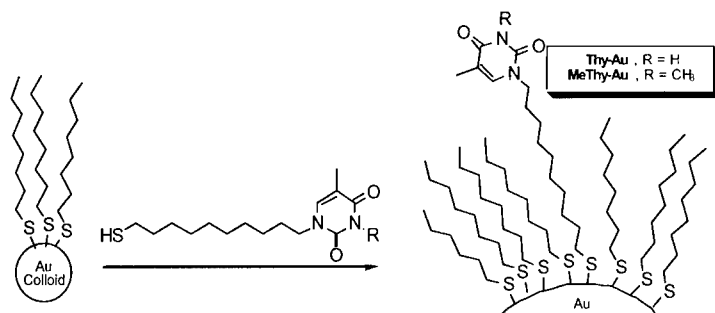
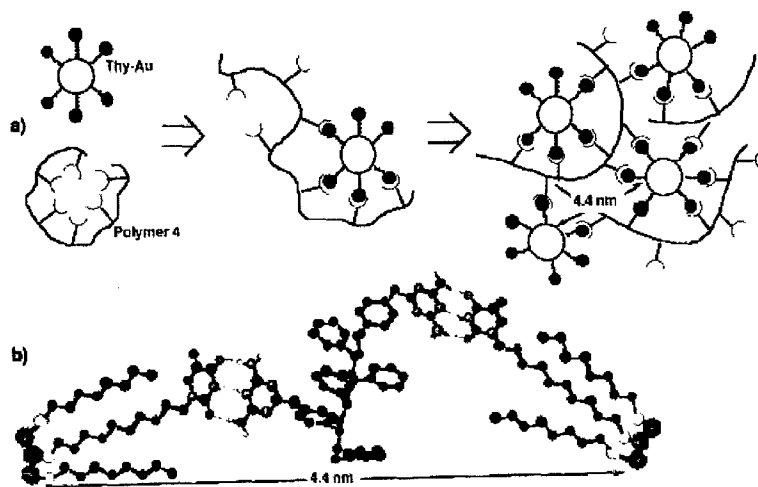


Figure 2. Preparation of **Thy-Au** and **MeThy-Au**.

Addition of polymer **1** to concentrated solutions of **Thy-Au** in non-competitive solvents such as dichloromethane and chloroform resulted in rapid formation of a black solid. In contrast, no precipitation was observed upon addition of **1** to the control colloid **MeThy-Au**. The lack of aggregation observed in the control system demonstrates that the precipitation observed upon the addition of **1** to **Thy-Au** was the result of specific hydrogen bond interactions between the colloid thymines and the polymer triazines.

To provide control of the aggregation process, polymer **1** and **Thy-Au** were mixed in dilute dichloromethane solution, with precipitation proceeding over a 96 h period. The resulting solid was insoluble in non-polar solvents, but >80% could be dissolved in polar media such as methanol and tetrahydrofuran (THF). Small angle x-ray scattering (SAXS) was used to characterize the Au particles *in situ* before and after this aggregation using Ni-filtered Cu K $\alpha$  radiation. After polymer **4**-induced aggregation, the SAXS plot of the precipitates exhibited a distinct maximum at  $Q = 0.94 \text{ nm}^{-1}$  characteristic of a defined separation distance between neighboring Au particles. After background subtraction, the center-to-center distance of Au particles was determined to be  $6.4 \pm 0.3 \text{ nm}$  in the polymer **1**-**Thy-Au** aggregate, corresponding to a 4.4 nm interparticle distance. Significantly, a sharp increase in the scattering was observed at small  $Q$ , suggesting the presence of larger scale structure (>20 nm) beyond instrumental resolution.

A model for the self-assembly observed in the aggregated structure is shown in Figure 3a. In non-polar solvents, polymer **1** folds into a highly compact structure due to intramolecular hydrogen bonds between the triazines. Multivalent interactions of polymer **1** with **Thy-Au** induce the unfolding of the compact structure of **1**, exposing further triazine recognition units. This allows polymer **1** to interact with further **Thy-Au** units, propagating the assembly process.



**Figure 3.** Proposed mechanism for **Thy-Au**-polymer 1 aggregation. a) Polymer mediated self-assembly of **Thy-Au** with experimentally determined interparticle distance shown. b) Proposed polymer 1-**Thy-Au** self-assembled structure (AMBER forcefield), with computationally predicted interparticle distance shown.

Insight into the structure of the polymer 4-**Thy-Au** aggregate was obtained through molecular modeling (Figure 3b). Using a configuration of the polymer chain that spans the gold particles, a particle-particle distance of 4.4 nm is obtained, agreeing very well with the distance of  $4.4 \pm 0.3$  nm determined by SAXS. This provides a working model for the polymer conformation between the Au-Au particles. The influence of polymer molecular weight, polymer functionalization, particles size, and particle functionalization on the self-assembly process is currently under investigation.

Proof of the large-scale ordering suggested by SAXS was obtained using transmission electron microscopy (TEM). Micrographs of the THF-soluble fraction of the polymer 4-**Thy-Au** precipitate reveal the formation of large highly regular, spherical clusters with diameters of  $97 \text{ nm} \pm 17 \text{ nm}$  in diameter. These clusters are comprised of 3000-7000 individual nanoparticles per microsphere. Significantly, the self-assembled microspheres are stable in polar solvents known to disrupt hydrogen bond interactions, providing further evidence that the macrostructure is stabilized by polyvalent polymer-colloid interactions. Roughly spherical aggregates of similar dimensions ( $\sim 60 \text{ nm}$ ) were obtained from 6 nm analogs of **Thy-Au** and polymer 1, demonstrating the applicability of our polymer-mediated approach to the assembly of different size nanoparticle subunits.

Self-assembly processes are governed by a balance of entropic and enthalpic effects, making them highly temperature dependent. This temperature dependence is manifested by more efficient recognition processes at lower temperatures,<sup>21</sup> a modification that would be expected to yield larger aggregate structures. Investigations of temperature effects on the preparation of the aggregates yielded intriguing results consistent with this prediction. TEM micrographs of the precipitate formed at  $-20^\circ\text{C}$  revealed the formation of *microscale* ( $0.5\text{-}1 \text{ }\mu\text{m}$ ) discrete spherical

particles, comprised of  $6 \times 10^5$ - $5 \times 10^6$  individual Thy-Au units. These microscale particles are among the most complex synthetic self-assembled structures known, demonstrating the thermal control of aggregate size using the 'bricks and mortar' methodology.

In addition to controlling the size of the aggregates, temperature dramatically affects the morphology of the resulting ensembles. At 10°C, networks were formed, as opposed to the discrete structures observed at higher and lower temperatures. This suggests that network formation is an intermediate process in the formation of the giant assemblies at -20 °C. the individual assemblies within these networks remained spherical, although their sizes are more highly dispersed. We are currently investigating methods aimed at achieving control over the size and the geometry of these networks, which would allow the fabrication of rod- and wire-like structures for incorporation in nanoscale constructs.

## ACKNOWLEDGEMENTS

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